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CHEMISTRY OF METHYLGALLIUM(III) COMPOUNDS IN PROTIC  
SOLVENTS(U) STATE UNIV OF NEW YORK AT BUFFALO DEPT OF  
CHEMISTRY O T BEACHLEY ET AL 10 NOV 86 TR-18  
N00014-78-C-0562

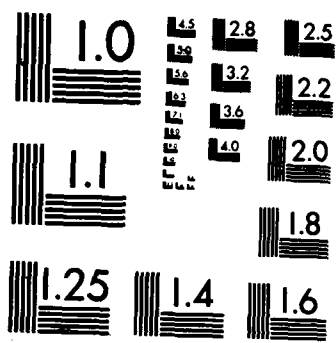
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XEROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Distribution list enclosed	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION State University of New York at Buffalo	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Buffalo, NY 14214		7b. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N0014-78C-0562	
8c. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. NR	PROJECT NO. 053
		TASK NO. 686	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Chemistry of Methylgallium(III) Compounds in Protic Solvents			
12. PERSONAL AUTHOR(S) O. T. Beachley, Jr., R. U. Kirss, R. J. Bianchini, T. L. Royster			
13a. TYPE OF REPORT Technical Report	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) 14 November, 1986	15. PAGE COUNT 16
16. SUPPLEMENTARY NOTATION To be published in "Organometallics"			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Gallium compounds, Methylation of gallium(III), Methylgallium compounds	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>The chemical properties of as well as routes to the formation of methylgallium(III) compounds in aqueous acidic solutions and in other protic solvents have been investigated. Aqueous perchloric acid solutions of <math>\text{Me}_2\text{GaClO}_4</math> at room temperature are surprisingly resistant to hydrolytic cleavage of the gallium-carbon bond. Only 14% of the available methyl groups of <math>\text{Me}_2\text{GaClO}_4</math> when dissolved in 0.0171 M <math>\text{HClO}_4</math> are converted to <math>\text{CH}_4</math> after a three month time period. In contrast, <math>\text{Me}_2\text{GaClO}_4</math> undergoes a significantly faster methyl transfer reaction with <math>\text{Ga}(\text{ClO}_4)_3</math> in aqueous <math>\text{HClO}_4</math> solution to form <math>\text{MeGa}^{+2}_{(\text{aq})}</math> which in turn hydrolyzes to form <math>\text{Ga}^{+3}_{(\text{aq})}</math> and methane. Approximately 36% of the initially available methyl groups form <math>\text{CH}_4</math> in three months. The dimethylgallium cation also methylates <math>\text{Hg}^{+2}_{(\text{aq})}</math> to form <math>\text{MeGa}^{+2}_{(\text{aq})}</math> and <math>\text{MeHg}^{+}_{(\text{aq})}</math> in aqueous solution but <math>\text{Me}_2\text{Ga}^{+}_{(\text{aq})}</math> does not react with <math>\text{Al}^{+3}_{(\text{aq})}</math>, <math>\text{Zn}^{+2}_{(\text{aq})}</math> or <math>\text{Na}^{+}_{(\text{aq})}</math>. In a second series of experiments the methylation of gallium(III)</p>			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL O. T. Beachley, Jr.		22b. TELEPHONE (Include Area Code) 716-831-3266	22c. OFFICE SYMBOL

19. ABSTRACT (continued)

by  $\text{Me}_2\text{Co}(\text{BDMl}, 3 \text{ pn})$  was investigated in ethanol and acetone solutions by using UV titration and  $^1\text{H}$  NMR data. The observed stoichiometry of the reaction requires one mol of  $\text{Ga}(\text{ClO}_4)_3$  for every two mols of  $\text{Me}_2\text{Co}(\text{BDMl}, 3 \text{ pn})$ . The identified products are  $\text{Me}_2\text{Ga}^{+}$  and  $\text{MeCo}(\text{BDMl}, 3 \text{ pn})^{+}$ . In contrast, gallium(III) is not methylated by methylcobalamin in aqueous solution.

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OFFICE OF NAVAL RESEARCH  
Contract N-00014-78-C-0562  
Task No. NR 053-686  
TECHNICAL REPORT NO. 18

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Prepared for Publication

in

Organometallics

State University of New York at Buffalo  
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14, November 1986

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Chemistry of Methylgallium(III) Compounds in Protic Solvents

by

O. T. Beachley, Jr.,\* R. U. Kirss, R. J. Bianchini, T. L. Royster

Abstract

The chemical properties of as well as routes to the formation of methylgallium(III) compounds in aqueous acidic solutions and in other protic solvents have been investigated. Aqueous perchloric acid solutions of  $\text{Me}_2\text{GaClO}_4$  at room temperature are surprisingly resistant to hydrolytic cleavage of the gallium-carbon bond. Only 14% of the available methyl groups of  $\text{Me}_2\text{GaClO}_4$  when dissolved in 0.0171 M  $\text{HClO}_4$  are converted to  $\text{CH}_4$  after a three month time period. In contrast,  $\text{Me}_2\text{GaClO}_4$  undergoes a significantly faster methyl transfer reaction with  $\text{Ga}(\text{ClO}_4)_3$  in aqueous  $\text{HClO}_4$  solution to form  $\text{MeGa}^{+2}_{(\text{aq})}$  which in turn hydrolyzes to form  $\text{Ga}^{+3}_{(\text{aq})}$  and methane. Approximately 36% of the initially available methyl groups form  $\text{CH}_4$  in three months. The dimethylgallium cation also methylates  $\text{Hg}^{+2}_{(\text{aq})}$  to form  $\text{MeGa}^{+2}_{(\text{aq})}$  and  $\text{MeHg}^{+}_{(\text{aq})}$  in aqueous solution but  $\text{Me}_2\text{Ga}^{+}_{(\text{aq})}$  does not react with  $\text{Al}^{+3}_{(\text{aq})}$ ,  $\text{Zn}^{+2}_{(\text{aq})}$  or  $\text{Na}^{+}_{(\text{aq})}$ . In a second series of experiments the methylation of gallium(III) by  $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$  was investigated in ethanol

and acetone solutions by using UV titration and  $^1\text{H}$  NMR data. The observed stoichiometry of the reaction requires one mol of  $\text{Ga}(\text{ClO}_4)_3$  for every two mols of  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ . The identified products are  $\text{Me}_2\text{Ga}^+$  and  $\text{MeCo}(\text{BDM1,3 pn})^+$ . In contrast, gallium(III) is not methylated by methylcobalamin in aqueous solution.

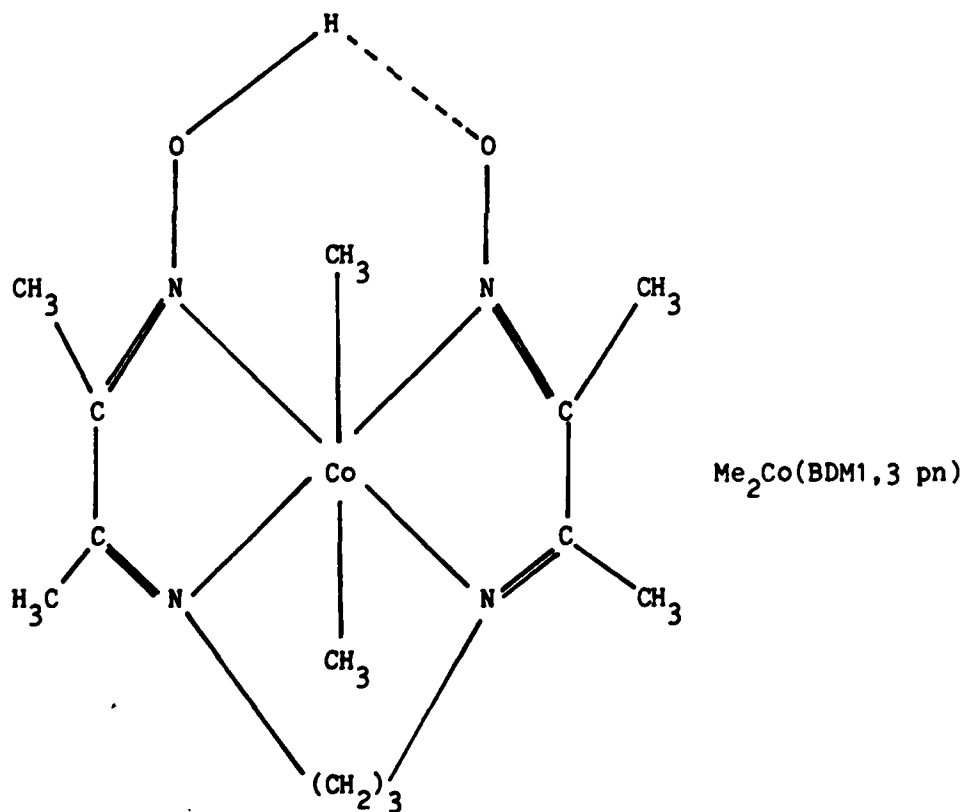
### Introduction

Methylgallium compounds can exist in aqueous solution<sup>1</sup> and these solutions are exceedingly toxic.<sup>2,3</sup> The inorganic derivatives of gallium are also poisonous.<sup>3</sup> However, relatively little is known about the hydrolytic stability, the chemical reactions or the modes of formation of methylgallium compounds in aqueous solution. The hydrolysis of trimethylgallium is very rapid until the first methyl group has been removed and then further hydrolysis becomes slow.<sup>1,4,5</sup> The removal of the second and third methyl groups has been described as being particularly slow.<sup>1,4,5</sup> For example, the reaction of a diethylether solution of  $\text{Me}_3\text{GaOEt}_2$  with a slight excess of water gives  $\text{Me}_2\text{GaOH}$ , which in turn reacts readily with both aqueous acids and bases at room temperature without rupture of the gallium carbon bonds.<sup>5</sup> No methane evolution<sup>5</sup> was reported when either excess  $\text{HNO}_3$ ,  $\text{HClO}_4$  or  $\text{NaOH}$  was added to  $\text{Me}_2\text{GaOH}$ . However, after the resulting solutions had been at room temperature for several hours, very small quantities of a gas were observed.<sup>5</sup> No further details regarding the extent of hydrolysis or the reaction products have been described in the literature.

The presence of toxic organometallic compounds in the aqueous environment has prompted numerous studies of reactions of metal ions with a variety of methylcobalt complexes. Mercury(II),<sup>6,7</sup> chromium(II)<sup>8</sup> and thallium(III)<sup>9</sup> have been observed to react with either [bis(diacetylmonooximeimino)1,3propane]dimethylcobalt(III) [ $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$ ] or bis(dimethylglyoximate)monomethylcobalt(III) to form  $\text{MeHg}^+$ ,  $\text{MeCr}^{+2}$  and  $\text{MeTl}^{+2}$ , respectively. Zinc(II), cadmium(II), and lead(II) also react with 2 mols of  $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$  in isopropanol to initially form  $\text{ZnMe}_2$ ,  $\text{CdMe}_2$  and  $\text{PbMe}_2$ , respectively, which then rapidly hydrolyze in the reaction solvent to liberate two mols of methane per mol of metal.<sup>10</sup>



The increasing importance of methylgallium compounds to the electronics industry as well as the potential presence and impact of methylgallium compounds in the environment lead us to study the chemical properties of methylgallium compounds in aqueous solution and in protic solvents. In this paper we report the results of our investigations of the hydrolytic stability of methylgallium compounds in dilute perchloric acid solution and of methyl transfer reactions between aqueous solutions of dimethylgallium(III) cations and gallium(III), aluminum(III) and zinc(II) perchlorate salts and mercury(II) nitrate. Secondly, we report on the



methylation of gallium(III) by Me<sub>2</sub>Co(BDM1,3 pn) in protic solvents. Our results demonstrate that aqueous solutions of dimethylgallium(III) cations are stable to hydrolysis of the gallium-carbon bond over a limited time

period but methyl transfer reactions can occur between  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  and  $\text{Ga}^{+3}_{(\text{aq})}$  and  $\text{Hg}^{+2}_{(\text{aq})}$ . Furthermore,  $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$  reacts with gallium(III)perchlorate in a 2:1 stoichiometry in ethanol solution to produce  $\text{Me}_2\text{Ga}^+$  as the only methylgallium(III) product. These reactions represent the first examples of the methylation of gallium(III) in protic solvents.

### Experimental

General. All of the compounds used in these studies, with the exception of trimethylgallium diethyletherate, were handled on the laboratory bench top. Trimethylgallium diethyletherate was prepared from  $\text{GaCl}_3$  and the methyl Grignard reagent in diethyl ether under an argon atmosphere. Dimethylgallium hydroxide was prepared from isolated and purified  $\text{Me}_3\text{Ga}\cdot\text{OEt}_2$  and water in diethyl ether at room temperature.<sup>5</sup> Dimethylgallium perchlorate<sup>5</sup> was prepared from  $\text{Me}_2\text{GaOH}$  and  $\text{HClO}_4$ . The cobalt complex,  $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$ , was prepared from  $\text{Co}(\text{BDM}1,3 \text{ pn})[\text{ClO}_4]_2$  using previously published methods.<sup>10,11</sup> The formation of  $\text{CH}_4$  from the hydrolysis of methylgallium(III) compounds was confirmed after isolation by fractional vacuum distillation and identification by vapor pressure measurements at  $-196^\circ\text{C}$  (10 mm).

Spectral Measurements. Infrared spectra were recorded in the range 4000 to  $250 \text{ cm}^{-1}$  by using either a Perkin-Elmer 457 or 683 spectrometer. Spectra of solids were observed as Nujol mulls using KBr or CsI windows. Ultraviolet spectra were recorded by using a Perkin-Elmer 575 UV-visible spectrometer and 1 cm quartz cells. Proton NMR spectra were recorded by using a Varian EM-390 spectrometer. Chemical shifts are reported in  $\delta$  units (ppm) with internal references of benzene ( $\delta$  7.13) or sodium 3-(trimethylsilyl)-1-propane sulfonate ( $\delta$  0.00). The following chemical shifts (reference benzene 7.13 ppm) of starting materials were observed:  $\text{Me}_2\text{GaOH}(\text{acetone-}d_6)$  -0.56(Me,s), 4.28(H,s);  $\text{Me}_2\text{Ga}(\text{ClO}_4)(\text{acetone-}d_6)$  -0.29(Me,s);  $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})(\text{acetone-}d_6)$  -0.19(Me,s), 1.94(s), 1.84(m), 2.04(s), 4.52(s).

Determination of Hydrolytic Stability of  $\text{Me}_2\text{GaClO}_4$  in Aqueous Solutions by Measuring the Evolved Methane. The hydrolytic stability of an aqueous

acidic solution of  $\text{Me}_2\text{GaClO}_4$  was monitored by measuring the evolved  $\text{CH}_4$  by using a Toepler pump-gas buret assembly. The following data were observed for a solution of 2.23 mL which was 0.994 M  $\text{Me}_2\text{GaClO}_4$  (2.217 mmol), 0.0171 M  $\text{HClO}_4$  and 1.27 M acetone, [Time, (mmol  $\text{CH}_4$ , % available methyl groups converted to  $\text{CH}_4$ )]: 6 days (0.0629, 1.42), 13(0.121, 2.73), 20(0.166, 3.74), 27(0.210, 4.74), 34(0.254, 5.73), 48(0.356, 8.02), 105(0.647, 14.6).

In a second series of experiments, the methane evolved from an aqueous solution of 2.96 mL which was 1.02 M  $\text{Me}_2\text{GaClO}_4$  (3.008 mmol), 0.884 M  $\text{Ga}(\text{ClO}_4)_3$  (2.617 mmol), 0.0164 M  $\text{HClO}_4$  and 1.00 M acetone was investigated. The following measurements of evolved  $\text{CH}_4$  were observed: [Time (mmol  $\text{CH}_4$ , % available methyl groups converted to  $\text{CH}_4$ )]: 6 days (0.157, 2.61), 13(0.336, 5.59), 20(0.478, 7.94), 27(0.610, 10.1), 34(0.761, 12.6), 48(1.12, 18.6), 76(1.93, 32.1), 103(2.22, 36.9).

Determination of Hydrolytic Stability of  $\text{Me}_2\text{GaClO}_4$  in Aqueous Solution by Using  $^1\text{H}$  NMR Spectroscopy. The hydrolytic stability of  $\text{Me}_2\text{GaClO}_4$  contained in sealed NMR tubes was evaluated using  $^1\text{H}$  NMR spectral data. For one series of experiments an aqueous solution which was 1.25 M  $\text{Me}_2\text{GaClO}_4$ , 0.020 M  $\text{HClO}_4$  and 1.25 M acetone was prepared. The relative intensity of the single line due to  $\text{Me}_2\text{GaClO}_4$  versus the line due to acetone was monitored over a period of 150 days. The following data were observed: Time (Integration ratio  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ /acetone): 0 days (1.0), 0.79 (0.95), 1.01 (1.0), 2.04 (0.86), 5.96 (0.96), 13.00 (0.99), 14.00 (0.96), 34.00 (0.99), 150.00 (1.0). After 150 days, an extremely small line due to  $\text{MeGa}^{2+}_{(\text{aq})}$  was just barely visible in the spectrum.

For a second series of experiments an aqueous solution which was 1.12 M  $\text{Me}_2\text{GaClO}_4$ , 0.969 M  $\text{Ga}(\text{ClO}_4)_3$ , 1.12 M acetone and 0.0179 M  $\text{HClO}_4$  was monitored over a period of 150 days. During the course of this study, the

$^1\text{H}$  NMR line due to  $\text{Me}_2\text{Ga}^+(\text{aq})$  decreased in intensity and a new line due to  $\text{MeGa}^{2+}$  appeared but never became very large relative to the line due to acetone. The following data were observed: Time (Integration ratio  $\text{Me}_2\text{Ga}^+(\text{aq})/\text{acetone}$ ;  $\text{MeGa}^{2+}/\text{acetone}$ ): 0 days (0.92; 0); 0.79 (0.89; 0.027); 1.01 (0.95; 0.025); 2.04 (0.90; 0.024); 5.96 (0.85; 0.063); 13.00 (0.74; 0.11); 34.00 (0.62; 0.17); 150.00 (0.042; 0.31).

In order to determine the effects of other metal perchlorate salts on the hydrolytic stability of  $\text{Me}_2\text{Ga}^+(\text{aq})$ , saturated aqueous solutions of  $\text{Me}_2\text{GaClO}_4$  containing 0.0912 M  $\text{HClO}_4$  were mixed with aqueous solutions of  $\text{Al}(\text{ClO}_4)_3$ ,  $\text{Zn}(\text{ClO}_4)_2$  and  $\text{NaClO}_4$ . The  $^1\text{H}$  NMR spectrum of these resulting solutions were monitored over a 150 day time period. The line due to  $\text{Me}_2\text{Ga}^+(\text{aq})$  did not decrease in intensity and no new lines suggesting the formation of  $\text{MeGa}^{2+}(\text{aq})$  or any other methylmetal species appeared.

Methyl Transfer Reactions Between  $\text{Me}_2\text{GaClO}_4$  and  $\text{Hg}(\text{NO}_3)_2$  in Aqueous  $\text{HClO}_4$  Solution. The reaction between  $\text{Me}_2\text{GaClO}_4$  and  $\text{Hg}(\text{NO}_3)_2$  in aqueous perchloric acid was monitored by means of a  $^1\text{H}$  NMR spectral titration. To an NMR tube which contained one ml of saturated  $\text{Me}_2\text{GaClO}_4$  solution in 0.0912 M  $\text{HClO}_4$  was added 0.173 M  $\text{Hg}(\text{NO}_3)_2$  dropwise. The  $^1\text{H}$  NMR spectrum was recorded after each  $\text{Hg}^{2+}$  addition. The data support the formation of  $\text{MeGa}^{2+}(\text{aq})$  and  $\text{MeHg}^+(\text{aq})$  (see Results and Discussion).

UV Spectral Titrations. Solutions of  $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$  in absolute ethanol (0.203 to 0.292 mM) were titrated with 4.14 mM  $\text{Ga}(\text{ClO}_4)_3$  in absolute ethanol in 0.50 mL increments. The extent of reaction was monitored by following the change in the UV spectrum in the 390 to 500 nm range of a sample contained in 1-cm quartz cells after equilibrium was established. The addition of  $\text{Ga}(\text{ClO}_4)_3$  was discontinued after at least three additions caused no change in the absorbance at 412 nm. The purity of  $\text{Me}_2\text{Co}(\text{BDM}1,3$

pn) was verified before each titration by recording the spectrum, noting the presence of the absorption at 412 nm characteristic of  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  as well as the absence of the absorption at 470 nm characteristic of  $\text{MeCo}(\text{BDM1,3 pn})^+$  and calculating the extinction coefficient of  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ . Similar UV titrations were studied in order to detect a potential reaction between methylcobalamin and  $\text{Ga}(\text{ClO}_4)_3$  in water.

Identification by  $^1\text{H}$  NMR Data of the Methylated Gallium Species From the Reaction of  $\text{Ga}(\text{ClO}_4)_3$  with  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ . A small quantity of  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  was dissolved in the desired solvent and the  $^1\text{H}$  NMR spectrum was recorded. Then, a sample of  $\text{Ga}(\text{ClO}_4)_3$  (0.50 mol/mol  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ ) was added and the spectrum was recorded a second time. The appearance of lines assigned to  $\text{MeCo}(\text{BDM1,3 pn})^+$ ,  $\text{Me}_2\text{Ga}^+$  and/or  $\text{MeGa}^{+2}$  were noted. After the spectrum showed no further change with time, a small quantity of a known solution of  $\text{Me}_2\text{GaClO}_4$  was added to verify the identity of the  $\text{Me}_2\text{Ga}^+$  line. These studies were carried out in both acetone- $\text{d}_6$  and ethanol- $\text{d}_6$ .

### Results and Discussion

Our experimental results demonstrate that aqueous acidic solutions of  $\text{Me}_2\text{GaClO}_4$ , which are reported<sup>5</sup> to contain  $\text{Me}_2\text{Ga}(\text{H}_2\text{O})_2^+$  and are represented as  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ , are surprisingly resistant to hydrolytic cleavage of the gallium-carbon bond to produce methane. In contrast,  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  undergoes a significantly faster methyl transfer reaction with  $\text{Ga}^{+3}_{(\text{aq})}$  in aqueous  $\text{HClO}_4$  solution to form  $\text{MeGa}^{+2}_{(\text{aq})}$  which in turn hydrolyzes to form  $\text{Ga}^{+3}_{(\text{aq})}$  and methane. Available data also suggest that  $\text{MeGa}^{+2}_{(\text{aq})}$  hydrolyzes much more rapidly than  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$ . The dimethylgallium cation also methylates  $\text{Hg}^{+2}_{(\text{aq})}$  to form  $\text{MeGa}^{+2}_{(\text{aq})}$  and  $\text{MeHg}^+_{(\text{aq})}$  but  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  does not react with  $\text{Al}^{+3}_{(\text{aq})}$ ,  $\text{Zn}^{+2}_{(\text{aq})}$  or  $\text{Na}^+_{(\text{aq})}$ . Conversely, gallium(III) is methylated by  $\text{Me}_2\text{Co}(\text{BDM}1,3 \text{ pn})$  to form  $\text{Me}_2\text{Ga}^+$  and  $\text{MeCo}(\text{BDM}1,3 \text{ pn})^+$  in ethanol and acetone solution. These methylation reactions of gallium represent the first examples in which gallium-carbon bonds are formed in protic solvents, including water.

The hydrolytic stability of methylgallium cationic species in  $\text{HClO}_4$  solution and the propensity of these cations to undergo methyl transfer reactions were monitored by measuring the evolved  $\text{CH}_4$  and by following the changes in the  $^1\text{H}$  NMR spectrum of related solutions. In the  $^1\text{H}$  NMR experiments, the intensities of the lines due to  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  (-0.35 ppm, referenced to sodium 3-(trimethylsilyl)propanesulfonate) and acetone were compared for 0.02M  $\text{HClO}_4$  solutions equimolar in  $\text{Me}_2\text{GaClO}_4$  and  $\text{Me}_2\text{CO}$ . The NMR signal due to  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  did not decrease in intensity over a period of five months and no other new signals of significant intensity appeared. In the experiments in which the  $\text{CH}_4$  was measured, only 0.0642 mmol of  $\text{CH}_4$  was formed after 6 days from 2.217 mmol of  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  and only 0.647 mmol  $\text{CH}_4$  was measured after 105 days, less than 15% of the available methyl groups. Both types of observations confirm that the hydrolysis of  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  in 0.02 M

$\text{HClO}_4$  is exceedingly slow. However, when a 0.018 M  $\text{HClO}_4$  solution equimolar in  $\text{Me}_2\text{GaClO}_4$ ,  $\text{Ga}(\text{ClO}_4)_3$  and  $\text{Me}_2\text{CO}$  was observed over the same time period, the intensity of the  $^1\text{H}$  NMR line due to  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  decreased with time and one new line at -0.14 ppm (referenced to sodium 3-(trimethylsilyl)propanesulfonate) due to  $\text{MeGa}^{+2}_{(\text{aq})}$  appeared in the spectrum, and grew slightly in intensity but never became very large relative to the acetone line. (The assignment of the new line to  $\text{MeGa}^{+2}_{(\text{aq})}$  is based on a comparison of the chemical shift of this line to a line in the spectrum of  $\text{MeGaCl}_2$  dissolved in a mixture of  $\text{HClO}_4$ , acetone and water at the identical pH.) The  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  line decreased to one half of its original intensity in approximately 80 days. However, the sum of the intensities of the lines due to  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  and  $\text{MeGa}^{+2}_{(\text{aq})}$  decreased relative to the intensity of the internal acetone sample. In the quantitative experiments of evolved  $\text{CH}_4$ , 0.157 mmol of  $\text{CH}_4$  was formed after 6 days from an acidic solution which initially contained 3.01 mmol of  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  and 2.617 mmol of  $\text{Ga}^{+3}_{(\text{aq})}$ . This quantity of  $\text{CH}_4$  is almost twice that observed for the solution which contained  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  as the only initial gallium species. Our observations are consistent with the occurrence of a methyl transfer reaction (equation 1) and the hydrolysis of the resultant  $\text{MeGa}^{+2}_{(\text{aq})}$  (equation 2). Thus,



$\text{MeGa}^{+2}_{(\text{aq})}$  is significantly more susceptible to gallium-carbon bond cleavage with methane formation than is  $\text{Me}_2\text{Ga}^+_{(\text{aq})}$  in aqueous perchloric acid solution.

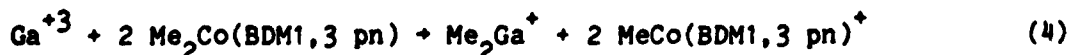


Methyl transfer reactions also occur between  $\text{Me}_2\text{Ga}^+(\text{aq})$  and  $\text{Hg}^{+2}_{(\text{aq})}$  in aqueous  $\text{HClO}_4$  solution but this reaction is significantly faster than methyl transfer between  $\text{Me}_2\text{Ga}^+(\text{aq})$  and  $\text{Ga}^{+3}_{(\text{aq})}$ . The intensity of the  $^1\text{H}$  NMR line due to  $\text{Me}_2\text{Ga}^+(\text{aq})$  at  $-0.35$  ppm, referenced to sodium 3-(trimethylsilyl)propanesulfonate, in a solution initially equimolar in  $\text{Me}_2\text{Ga}^+(\text{aq})$  and  $\text{Hg}^{+2}_{(\text{aq})}$  decreased to half of its original intensity in only 31 minutes and two new lines at  $1.08$  and  $-0.14$  ppm appeared in the spectrum. The line at  $1.08$  ppm is assigned to  $\text{MeHg}^+(\text{aq})$  by comparison with the literature<sup>12</sup> whereas the line at  $-0.14$  ppm is due to  $\text{MeGa}^+(\text{aq})$ . The observed



formation of  $\text{MeHg}^+(\text{aq})$  instead of  $\text{HgMe}_2$  is consistent with previously observed methylation reactions of mercury(II). Others<sup>9</sup> have also observed that it is more difficult to methylate  $\text{MeHg}^+(\text{aq})$  than  $\text{Hg}^{2+}_{(\text{aq})}$  due to the decreased electrophilic character of  $\text{MeHg}^+(\text{aq})$ . It is significant to note that mercury(II) acetate is also methylated<sup>13</sup> by  $\text{Me}_2\text{Tl}(\text{MeCO}_2)$ , another group 3 alkyl, to yield  $\text{MeHg}^+(\text{aq})$  and  $\text{MeTl}^{+2}_{(\text{aq})}$ .

Bis(diacetylmonoximeimino1,3propane)dimethylcobalt(III),  $\text{Me}_2\text{Co}(\text{BDM}1,3\text{pn})$ , methylates gallium(III) perchlorate and gallium(III) chloride in polar solvents. This reaction represents the first reported example of the formation of a dimethylgallium(III) species in a protic solvent. The stoichiometry of the reaction as shown by equation 4 is consistent with all UV titration data. In the UV titrations, absolute ethanol solutions of



$\text{Ga}(\text{ClO}_4)_3$  were added to ethanol solutions of  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ . The linear decrease in the absorbance at 412 nm, characteristic of  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$ ,<sup>10</sup> as well as the increase in the absorbance at 470 nm, characteristic of the methylcobalt(III) product,<sup>10</sup>  $\text{MeCo}(\text{BDM1,3 pn})^+$ , were used to determine the extent of reaction. A plot of the absorbance at 412 nm versus the mol ratio  $\text{Ga}^{+3}/\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  had a distinct break at 0.532 mole of  $\text{Ga}^{+3}$  per mole of  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  (Figure 1). The observation of only the absorbance at 470 nm<sup>10</sup> at the end of the titration demonstrates the formation of  $\text{MeCo}(\text{BDM1,3 pn})^+$  and precludes the possibility that both methyl groups are removed from cobalt.

The proposed stoichiometry of the  $\text{Ga}^{+3}-\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  reaction and the identity of the products are also supported by  $^1\text{H}$  NMR spectral data. The products observed after reaction were  $\text{MeCo}(\text{BDM1,3 pn})^+$  and  $\text{Me}_2\text{Ga}^+$ . The NMR spectrum of  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  in acetone is characterized by a sharp singlet at -0.16 ppm (referenced to benzene at 7.13 ppm) for the methyl groups bound to cobalt. This resonance disappeared as  $\text{Ga}(\text{ClO}_4)_3$  was added and two new sharp lines at 0.51 and -0.26 ppm due to methyl groups of  $\text{MeCo}(\text{BDM1,3 pn})^+$  and  $\text{Me}_2\text{Ga}^+$ , respectively, appeared. The identity of the species responsible for the -0.26 ppm line,  $\text{Me}_2\text{Ga}^+$ , was verified by examining the  $^1\text{H}$  NMR spectrum of the product mixture after the addition of a solution of pure  $\text{Me}_2\text{GaClO}_4$ . The stoichiometry of the methylation reaction of gallium(III) by  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  and identity of the reaction products were independent of the solvent, ethanol, acetone or acetonitrile, and the gallium(III) reactant,  $\text{Ga}(\text{ClO}_4)_3$  and  $\text{Ga}(\text{NO}_3)_3$ .

Gallium species other than simple solvated  $\text{Ga}^{+3}$  ions have also been shown to undergo methyl transfer reactions with  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  in acetone and ethanol solution. Anhydrous  $\text{GaCl}_3$  dissolves in ethanol and acetone but

the exact nature of the solubilized species is unknown. Therefore, the gallium(III) solute<sup>14</sup> will be referred to as  $[\text{GaCl}_n]^{(3-n)+}$ . These solutions react readily with  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  in a 1:2 stoichiometry to yield  $\text{MeCo}(\text{BDM1,3 pn})^+$  and a dimethylgallium(III) product according to data from UV spectroscopic titrations and  $^1\text{H}$  NMR studies. It is also significant that  $[\text{GaCl}_n]^{(3-n)+}$  undergoes a faster methyl transfer reaction with  $\text{Me}_2\text{Ga}^+$  in acetone than  $\text{Ga}^{+3}$  from  $\text{Ga}(\text{ClO}_4)_3$  does in water. The intensity of the  $^1\text{H}$  NMR line due to  $\text{Me}_2\text{Ga}^+$  decreased to one half intensity in 112 hours in the presence of excess  $[\text{GaCl}_n]^{(3-n)+}$  in acetone solution and a new line due to  $\text{MeGa}^{+2}$  appeared.

The methylcobalt(III) complex  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  is considered to be of high reactivity for the methylation of metal ions whereas methylcobalamin is significantly less reactive.<sup>10</sup> Since  $\text{Ga}^{+3}$  reacted so readily with  $\text{Me}_2\text{Co}(\text{BDM1,3 pn})$  to form  $\text{Me}_2\text{Ga}^+$ , the reactivity of methylcobalamin toward  $\text{Ga}(\text{ClO}_4)_3$  in aqueous solution was studied by UV titration experiments. However, no reaction occurred. The absorbance of the bands of methylcobalamin at 520 and 350 nm did not change significantly as an aqueous solution of  $\text{Ga}(\text{ClO}_4)_3$  was added. Thus, it is unlikely that exceedingly toxic methylgallium species will be formed directly by methylcobalamin methylation in the aqueous environment.

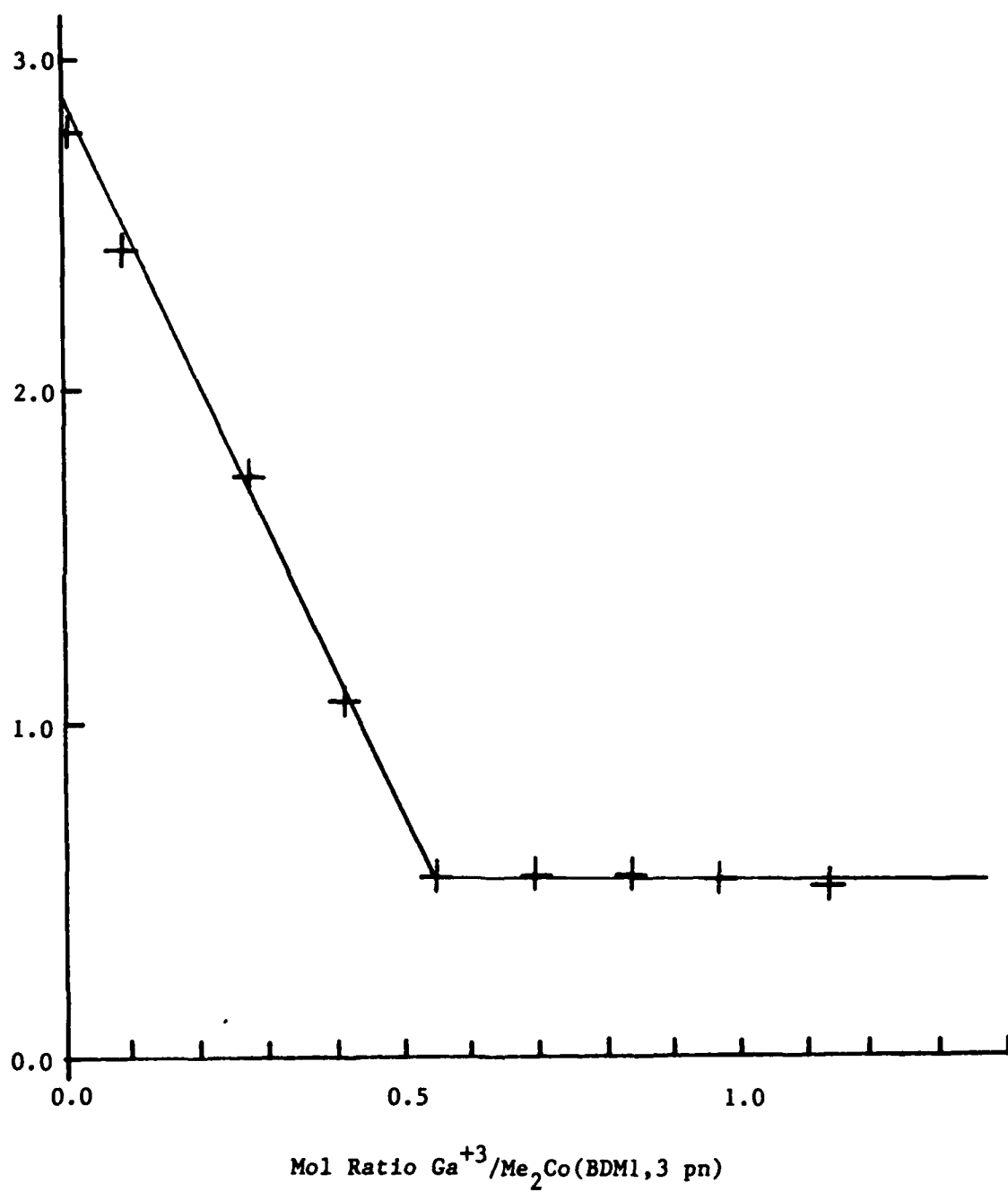
Acknowledgment. This work was supported in part by the Office of Naval Research.

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Figure 1

Titration of  $\text{Me}_2\text{Co}(\text{BDMl},3 \text{ pn})$  with  $\text{Ga}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$



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